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(71) Applicant

BP Chemicals Limited

(Incorporated in the United Kingdom)

Belgrave House, 76 Buckingham Palace Road,  
London, SW1W 0SU, United Kingdom

(72) Inventor

Hilda Adams Leiper

(74) Agent and/or Address for Service

Michael John Wilson  
BP International Limited, Patents & Agreements  
Division, Chertsey Road, Sunbury-on-Thames,  
Middlesex, TW16 7LN, United Kingdom

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## (54) Stabilizer composition

(57) Stabiliser compositions comprise (a) a phenolic or amine antioxidant (c) a metal deactivator and at least one of (b) a neutraliser and (d) an antioxidant which is a phosphorus containing compound or a thioether or disulphide. The compositions stabilise polymers such as polyolefins against oxidation. Compositions of (a), (b) and (c) and optionally (d) show synergistic oxidation resistance, while compositions of (a) (c) and (d) increase the tear strength of polyolefin films. The phenolic antioxidant is preferably sterically hindered. The amine is preferably a secondary aromatic amine or a hindered N-heterocyclic compound. The metal deactivator is preferably an hydrazide, oxalamide or a cyclic diazole or triazole, or a hindered phenol. The neutraliser may be a base, e.g. a tertiary amine, a piperidine, an inorganic basic oxide or hydroxide or a salt of a weak acid, e.g. calcium stearate, or preferably an inorganic anion exchanger in basic form, e.g. magnesium aluminium talcite. The phosphorus compound may be a phosphonite or phosphite ester.

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STABILIZER COMPOSITION

This invention relates to stabilizer compositions, in particular for use with polyolefins.

During the processing of ethylene polymers at high temperatures and during their use, they are subject to oxidative and thermal 5 attack leading to deterioration in their properties. Hitherto this deterioration has been reduced by use of stabilizers such as hindered phenols and/or phosphites. It has also been found that deteriorated molten polymers tend to form gels, which on extrusion provide bodies having non uniform properties.

10 Polyolefins can be melt extruded to form film, as such or in the form of tubes, which may subsequently be oriented mono or biaxially. Commercial conditions of melt mixing and extrusion, with high temperature and high shear rate, tend to reduce the tear strength of the film obtained often to more than half the figure for 15 film obtained under laboratory conditions. The susceptibility of polyolefins to oxidative and thermal degradation is retarded by addition of stabilizers such as hindered phenols and/or phosphites, but these additives may have insufficient effect on the film tear strength.

20 It has now been discovered how to increase the oxidative stability namely by use of a multi component stabilizer composition of hindered phenol or amine, neutralizer and metal deactivator.

25 It has now also been discovered how to increase the tear strength of polyolefin film, namely by use of an additive composition of a phenolic or amine antioxidant, a phosphorus

antioxidant and a metal deactivator.

The present invention provides a stabilizer composition which comprises (a) at least one phenolic or amine antioxidant, (c) a metal deactivator and at least one of (b) a neutralizer and (d) a antioxidant, which is a phosphorus containing compound preferably a phosphite ester or phosphonite ester, or a thioether or sulphide.

The present invention also provides a stabilized polyolefin composition which comprises a polyolefin and a stabilizer composition of the invention; the polyolefin composition usually gives a film of improved tear strength.

The phenolic or amino antioxidant is preferably an aromatic compound, which is an amine or hindered phenol.

The sterically hindered phenol, which is preferred, usually has at least one alkyl group eg of 1-6 carbons and especially 2 alkyl groups in an ortho position to the phenolic hydroxyl group. Secondary or especially tertiary alkyl groups are preferred such as isopropyl, isobutyl and isoamyl, but especially tert butyl. The aromatic compound may just have the hydroxy or amine group substituent, and alkyl substituents but preferably contains at least one other substituent, especially containing an ester group such as one with a fatty alkyl chain eg of 8-20 carbons. The other substituent is preferably a alkyloxycarbonyl alkylene group with 1-24 and especially 8-20 carbons in the alkyl group and 1-4 carbons in the alkylene group. The phenol (a) may also be an ester of a alcohol of 1-5 hydroxyl groups and 1-24 carbons especially 2-5 hydroxyl groups and 2-8 carbons such as pentaerythritol and a hindered-phenol-substituted carboxylic acid especially a substituted alkanoic acid of 1-6 eg 2-4 carbon atoms. The hindered phenol is usually free of enolizable groups such as -CONH- groups.

Examples of hindered phenols are 2,6 di-tertbutyl phenol, thio bisphenols such as bis (2-hydroxy-3-tert.butyl-5-methylphenyl) sulphide and bis-(2-methyl-4-hydroxy-5-tert.butylphenyl) sulphide, alkylidene bis phenols such as methylene and ethylidene bis-(methyl tert.butyl-2-or 4-phenols), hydroxybenzyl compounds such as 4-

hydroxy-2,6-ditert.butyl-benzyl compounds such as tris 2,4,5-(4-hydroxy-2,6-ditert.butylbenzyl) durene and amino phenols such as fatty acyl amino phenols and hydroxyphenyl propionates especially 3-[3,5-di-tert.butyl-4-hydroxyphenyl]-propionate esters such as the 5 monoester of octadecanol or the tetra ester of penta erythritol (eg as sold as IRGANOX 1010).

The amine antioxidant is preferably aromatic and may be hindered with an alkyl group ortho to the amine group but is preferably a secondary aromatic amine especially a bis(aromatic) 10 amine, wherein the aromatic groups are the same or different. Examples of amines are secondary aromatic amines eg of 6-50 or 14-35 carbon atoms such as bis (4-alkyl phenyl) amines or bis [4-(2'-phenylpropylidene) phenyl] amine. Other amine antioxidants are hindered N-heterocyclic compounds with at least one alkyl group eg 15 of 1-6 carbon atoms and especially 2 alkyl groups on a ring carbon atom adjacent to N-heterocyclic atom. Secondary or tertiary alkyl groups are preferred such as isopropyl, isobutyl and isoamyl, but especially tertbutyl. Examples of the heterocyclic compounds are substituted piperidines, especially 2,6-dialkyl piperidines and 20 their N-alkyl substituted derivatives.

Component (b) which is preferably present is a neutralizer. Organic or inorganic compounds eg bases may be used. The organic base is usually an amine preferably a tertiary amine such as an aliphatic one eg of 3 - 20 carbon atoms which is especially an alkyl 25 or hydroxyalkyl one with 1 - 6 carbons such as tripropylamine, tributylamine, triethanolamine and triisopropanolamine. Other organic bases are cyclic amines such as piperidine and C and/or N substituted piperidines; preferred compounds are 2,6 dialkyl piperidine and its N-alkyl substituted derivatives. When 30 antioxidant (a) is an amine rather than a phenolic antioxidant, the neutralizer is preferably an inorganic basic compound. The inorganic basic compound is usually from a non transition metal of 1-3 valency especially of Group 1A, 2A, 2B, 3A or 4B of the Periodic Table such as sodium, magnesium, calcium, zinc, aluminium or lead; 35 calcium compounds are preferred. The basic compounds are usually

oxides, hydroxides or salts with weak acids eg carboxylic acids of 2-20 eg 10-20 carbon atoms such as acetic and stearic acid. Calcium stearate is preferred. The basic compound is usually a solid and preferably itself or its hydrochloride salt is non volatile and 5 stable at polyolefin processing temperatures; advantageously it has a particle size of less than 100 micrometres, such as 1-10 micrometres.

Very advantageously the component (b) is an anion exchanger in basic form, in particular an inorganic anion exchanger in basic form 10 eg as the hydroxide or especially the carbonate form. The anion exchanges is usually of mean particle size less than 10 micrometres especially less than 1 micrometre such as 0.05-10 or 0.1-1 micrometre. Preferred is magnesium aluminium talcite ( $Mg_{4.5} Al_2 (OH)_{13} CO_3 \cdot 3.5H_2O$ ), which has preferably been treated with a surface 15 active agent such as that sold by Kyowa Chemicals Industry Co Limited under the trademark DHT-4A. The basic compound is believed to remove the acid and/or residual chloride from the polyolefin composition.

A mixture of the basic compounds may be used eg the anion 20 exchanger and the metal carboxylate, such as in weight proportions of 10-90:90-10, especially 20-50:50-80.

The metal deactivator (c) forms complexes with metals, especially transition metals and may reduce their catalytic effect 25 on polymer oxidation. It is a metal complexant usually at least bi or tri dentate and forms 4-6 membered rings with the metal. The deactivators usually contain 2 CONH groups usually combined in oxalamide or hydrazide form, though if desired one of the CONH groups may be in the form of a  $-C(=N)-N-$  component of a heterocyclic ring such as a diazole or triazole. The deactivator is usually of 30 formula:



Wherein R represents an aromatic group eg of 6-20 carbon atoms, Z represents a divalent organic group eg of 1 - 16 carbon atoms, X represents a  $-CONH-$  or  $NHCO$  group, and Y represents a group 35 of formula  $-X^1-(Z^1-X^2-X^3)_b-(Z^2)_c-R^1$  or a heterocyclic ring with a

$-C(=N)-N$ -group, wherein each of  $X^1$ ,  $X^2$  and  $X^3$ , which are the same or different, represents a CONH or NHCO group, and each of  $Z^1$  and  $Z^2$  which are the same or different represents a divalent aliphatic group eg of 1-10 carbon atoms, and  $R^1$  represents an aromatic group, eg of 6 - 20 carbon atoms, and each of a, b and c, which may be the same or different, represents 0 or 1. Preferably each of R and  $R^1$  is of 6 - 16 carbon atoms and usually contains 1 - 3 substituents preferably at least one of which is a phenolic hydroxyl or alkoxy group of 1 - 6 carbon atoms or alkyl group eg of 1 - 6 carbon atoms such as methyl ethyl or especially tert butyl. Advantageously the hydroxyl or alkoxy group is in a ring position ortho or para to the group Z or  $Z^2$  (if present) or group X or  $X^3$  and preferably ortho to one or more alkyl groups. When a or c is 0, the group R or  $R^1$  respectively is bonded directly to group X or  $X^3$  respectively but otherwise the bonding is via spacer group Z or  $Z^2$ , which is preferably a divalent aliphatic group of 1 - 18 carbon atoms such as alkylene of 1 - 4 carbons eg methylene or ethylene or an azomethine group ( $-CH=N-$ ) or alkylene group interrupted by one or more oxa or aza and/or carbonyl groups such as an alkylene carboxy alkylene group eg with 1 - 12 or 1 - 3 carbons in each alkylene group.  $Z^1$  may be as defined for Z or  $Z^2$  but is preferably an alkylene group of 2 - 10 carbons such as polymethylene with 3 - 7 methylene groups. The heterocyclic ring representing Y may be a 1,2,4-triazol - 3 - yl or pyrazol - 3 - yl group. Each of the pairs  $X-X^1$ , and  $X^2-X^3$  if present independently preferably represents an oxalamide or hydrazide group. The deactivator may be asymmetrical but is preferably symmetrical.

The metal deactivator may be of formula  $R^2-NH-CO-R^3$ , wherein  $R^2$  is an aromatic group eg of 6 - 20 carbon atoms and preferably as described for R above, or is an  $R^4CONH$  or  $R^4CH=N-$  group or is a cyclic diazole or triazole group eg a 1,2,4-triazol - 3 - yl group, and  $R^3$  is a  $CONHR^4$  group or contains an aromatic group, eg of 6 - 20 carbon atoms such as described for R above or an alkyl group eg of 1 - 18 carbon atoms, and  $R^4$  is an aromatic group eg of 6 - 20 carbon atoms, preferably as described for R above.

Preferably b is 0 so the deactivator contains one pair of CONH or NHCO groups especially in oxalamide or hydrazide form.

Preferably when X-X<sup>1</sup> represents an oxalamide group, a is 0 or 1, Z and Z<sup>2</sup> are alkylene or alkylene carboxyalkylene or azomethine group and each of R and R<sup>1</sup> represents a phenyl, mono- or di-alkyl phenyl, alkoxyphenyl or mono or dialkyl-mono-hydroxyphenyl group especially a 3,5-dialkyl-4-hydroxy group. Preferably when X-X<sup>1</sup> represents a hydrazide group, a is 0 or 1, Z and Z<sup>2</sup> are alkylene and each of R and R<sup>1</sup> represents a hydroxyphenyl or mono-or di-alkyl mono hydroxyphenyl group especially a 3,5-dialkyl-4-hydroxy group.

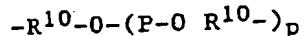
Particularly preferred compounds are 2,2' - oxamido - bis[ethyl-3-(3,5-di-tertiary-butyl-4-hydroxyphenyl) propionate] (eg as sold under the trademark NAUGARD XL-I), 2-ethoxy-5-tert.butyl (2'-ethyl bis oxanilide (eg as sold under the trademark SANDUVOR EPU) and oxaryl bis (benzylidene hydrazide (eg as sold under the trademark Eastman OABH), N,N'-bis[3-(3,5-di-tert.butyl-4-hydroxy phenyl] propion hydrazide (sold under the trademark IRGANOX MD1024) and decamethylene dicarboxy di salicyloyl hydrazide (sold under the trademark MARK CDA-6) and 3 - (salicyloyl)amino-1,2,4-triazole (sold under the trademark MARK CDA-1).

Even if the deactivator (c) is a hindered phenol, a further component (a) eg hindered phenol is needed.

Preferably the composition also contains a secondary antioxidant (d), which may preferably be a phosphorus containing compound such as a phosphite or phosphonite ester, or may be a thioether or disulphide.

The phosphorus antioxidant is usually an ester, with each P atom therein attached to at least 2 oxygen atoms in an ester linkage and attached also to another oxygen atom in an ester linkage or to a carbon atom or to a halogen eg F atom; thus phosphite phosphonite and halo phosphite esters are preferred. The phosphorus antioxidant is usually substantially free of P-OH groups. Examples of suitable phosphites are those of formula  $[R^5O-P(OR^6)O]_nR^7$  where n is an integer of 1 to 4 especially 1 or 2 each of R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup>, which may be the same or different, represents an alkyl group eg of 1-20 but

preferably 8-20 carbons such as decyl, dodecyl, tridecyl,  
 tetradearyl, cetyl or stearyl, or a cycloalkyl group eg of 5-9 carbon  
 atoms such as cyclohexyl, or an aryl group eg of 6-20 carbons eg an  
 aromatic hydrocarbyl group especially phenyl, optionally substituted  
 5 with 1 or 2 alkyl eg 1-6 carbon atom groups such as tert butyl, as  
 in di-tert butylphenyl or nonylphenyl. Preferably at least one and  
 especially 2 or 3 groups for  $R^5$ ,  $R^6$  and  $R^7$  represent aryl groups.  
 Alternatively  $R^6$  and  $R^7$  together represent a divalent residue  $R^8$   
 formed by removal of 2 hydroxyl groups from a 1,2 or 1,3 diol such  
 10 as an alkylene diol of 2-4 carbon atoms to give a compound of  
 formula  $R^5O_2P(O_2R^8)_n$ . Advantageously  $n$  is 2 and the phosphite is a di  
 or poly phosphite wherein  $R^5$  and  $R^6$  are as defined and  $R^7$  represents  
 a divalent residue  $R^9$  formed by removal of hydroxyl groups from a  
 diol eg of 2-20 carbons, such as a linear aliphatic diol (including  
 15 ether diols) eg mono or dipropylene glycol, or a dihydroxylic phenol  
 eg of 6-20 carbons, especially a phenol with 2 phenylene groups such  
 as bisphenol A.  $R^7$  may also represent a divalent group of formula



20 where  $p$  is 1-15 eg 2-10, and  $R^{10}$  is as defined for  $R^9$ .  $R^7$  as such  
 or together with  $R^6$  may also represent a tetra valent residue  $R^{11}$   
 formed by removal of 4 hydroxyl groups from a tetra hydroxyl  
 compound eg an aliphatic one of 4-8 carbon atoms such as  
 25 pentaerythritol; preferably the phosphite is of formula  $R^5O$   
 $P(O_2R^{11}O_2)POR^5$ . Instead of the phosphite a phosphonite of formula  
 $[R^5O(R^6O)P]_bR^4$  may be used wherein  $b$  is 1 or 2,  $R^5$  and  $R^6$  are as  
 defined above and  $R^4$  is an aliphatic group eg of 1-10 carbon atoms  
 or aromatic group eg aromatic hydrocarbyl group of 6-19 atoms  
 30 especially a phenyl or mono or dialkyl phenyl group in particular  
 mono- or di-tertiary butyl phenyl, especially in the ortho and/or  
 para positions, or  $R^4$  forms a divalent aliphatic group  $R^{12}$  eg of  
 1-10 carbon atoms or a divalent aromatic group such as an aromatic  
 hydrocarbyl group with 6-20 carbons such as phenylene eg  
 35 1,4-phenylene or biphenylene eg  $p,p'$ -biphenylene. Preferably the

phosphonite is of formula  $R^5O(R^6O)PR^{12}P(OR^6)OR^5$ . Advantageously the phosphite ester has at least two phosphite ester groups per molecule and a structural unit derived from at least one polyol of 2-4 hydroxyl groups, and especially contains both aliphatic-O-P and aromatic OP bonds. Examples of suitable phosphorus compounds are the tris (2,4-di tert-butyl) phenyl phosphite (sold as IRGAFOS 168), tris (nonylphenyl) phosphite, tri phenyl phosphite, (sold as DOVERPHOS 10), tris tridecylphosphite, (sold as DOVERPHOS 49), tetrakis (2",4"-di-tert.butylphenyl)-4,4'-biphenylene diphosphonite, (sold as IRGAFOS P-EPQ), bis(di-2,4-(tert butyl) phenyl diphosphite esters from pentaerythritol (sold as ULTRANOX 626), the distearyl diphosphite esters from pentaerythritol (sold as WESTON 618 or DOVERPHOS S680) the latter optionally with less than 2% eg 0.5 - 2% such as 1% of an aliphatic amine eg an alkanolamine of 6-20 carbon atoms such as tris(isopropanol) amine) (sold as DOVERPHOS S682), tetra phenyl di propylene glycol diphosphite (sold as DOVERPHOS II), tetra kis(stearyl) ester of 2,2-bis(4-hydroxyphenyl) propane diphosphonite (sold as DOVERPHOS 454) and the poly phosphite esters such as polydipropylene glycol phenyl polyphosphite with 4-10P atoms (sold as DOVERPHOS 12), and poly (2,2-bis(4 hydroxylphenyl) propane) alkyl polyphosphites, with 4-10 P atoms, wherein the alkyl group has an average of 15-16 carbon atoms (eg as sold as DOVERPHOS 613).

If desired, a phosphonite ester may be present as or comprising component (d). Examples of such esters which are substantially free of P-OH group are ones of formula  $[R^5O(R^6O)P]_bR^4$  wherein b is 1 or 2,  $R^5$  and  $R^6$  are as defined above and  $R^4$  is an aliphatic group eg of 1-10 carbon atoms or aromatic group eg aromatic hydrocarbyl group of 6-19 atoms especially a phenyl or mono or dialkyl phenyl group in particular mono- or di-tertiary butyl phenyl, especially in the ortho and/or para positions, or  $R^4$  forms a divalent aliphatic group  $R^{12}$  eg of 1-10 carbon atoms or a divalent aromatic group such as an aromatic hydrocarbyl group with 6-20 carbons such as phenylene eg 1,4-phenylene or biphenylene eg p,p'-biphenylene. Preferably the phosphonite is of formula  $R^5O(R^6O)PR^{12}P(OR^6)OR^5$ .

Examples of suitable phosphonite esters are tetrakis

(2",4"-di-tert.butylphenyl)-4,4<sup>1</sup>-biphenylene diphosphonite, (sold as IRGAFOS P-EPQ), and tetra kis(stearyl) ester of 2,2-bis(4-hydroxyphenyl) propane diphosphonite (sold as DOVERPHOS 454).

5 Instead of or as well as the phosphorus ester, the stabilizer composition can contain at least one sulphur containing antioxidant such as a thio ether eg a diaryl ether of 12-30 especially 16-24 carbon atoms, such as a bis(tertiary alkyl phenyl) sulphide which may optionally have at least one hydroxyl or other alkyl substituent 10 eg methyl or ethyl, especially with the sulphur and/or oxygen if present in the ortho position to the tertiary alkyl group such as a tertiary butyl group; 2,2'-thio-bis(4-methyl-6-tert.butyl phenol) and 4,4-thio bis(3-methyl-6-tert.butyl phenyl) are preferred. Other thio ethers are mercaptopropionate esters and the corresponding 15 disulphides eg bis(2-alkoxy carbonyl ethyl) sulphide and disulphide with 8-24 carbon atoms in the alkoxy group, which is especially lauryloxy or stearyloxy.

20 The compositions of the invention, especially those of (a), (b) and (c) and especially (d), may be used to stabilize polyolefins against oxidation, eg during processing in particular under conditions of very high shear and high temperature such as during conversion from powder to pellets, or during subsequent conversion to form artifacts in their final shape such as during melt mixing, moulding and extrusion such as to form film, fibres, pipes, bottles 25 and other containers. In particular the compositions may be used to reduce gel formation during melt processing and in extruded film. Such gels, apart from being unsightly, also constitute irregularities in the properties of the film.

30 The additive compositions of the invention especially those of (a), (c) and (d), may be used in polyolefins in order to increase the tear strength of film made from the polyolefin via commercial pelletization, moulding or extrusion conditions eg with high shear rates and temperatures such as 170-350° and especially about 300°C.

35 The polyolefins which can be stabilized by the compositions of the invention are usually ones containing metal residues, especially

transition metal residues such as titanium and/or chromium and/or iron and in amount of 10 - 500 ppm, and in particular acidic and/or chloride containing metallic residues eg with free hydrogen ion and/or chloride ion each possibly in amounts of 10 - 250 ppm. While 5 these residues are usually present in the polyolefin because of its mode of polymerization, they may result from accidental contamination in the production eg iron residues or intentional addition from compounds added for another purpose. Finally the metal residues may be introduced in use eg with copper such as the 10 use of copper metal imprinting.

Examples of suitable polyolefins are homo or copolymers of alpha olefins of 2 - 10 carbon atoms, in particular homo polymers of ethylene, or copolymers of ethylene with at least one or 2 alpha olefins of 3 - 10 carbon atoms such as propylene, butene-1, 15 n-hexene-1, 4-methylpentene-1 and octene-1, in particular with up to 30% or up to 20% (by weight of total monomer units) of the alpha olefin, such as 1 - 10% (as in LLDPE) or 10 - 20% (very low density polyethylene VLDPE). The polyolefin is preferably substantially linear and is preferably at least 5% crystalline and especially at 20 least 25% crystalline. Any polyolefin copolymer may be a random, block, sequential or end block copolymer. The polyolefin usually has a Specific Gravity of 0.86 to 0.98 eg 0.88 to 0.94. Examples of polyolefins are high density, linear low density and very low density poly ethylene. Blends of 2 or more polyolefins may be used.

25 The stabilizer compositions of the composition usually contain (in parts by weight, preferably per million based on the weight of polymer with which they are to be mixed, component (a) 5 - 10,000 eg 50 - 5,000 preferably 100 - 1,500, component (b) 0-20,000 such as 10 - 20,000 eg 100 - 7,500 preferably 300 - 3,000 component (c) 10 - 30 10,000 eg 50 - 2,500 preferably 50 - 1,500 component (d) 0 - 15,000 eg 100 - 15,000 preferably 200 - 5,000 or - 7500 such as 300-2000, and component (f) fluoro polymer, (as further described below), 0 - 10,000 eg 50 - 10,000 preferably 100 - 2,000. Particularly preferred are compositions containing 150 - 800 parts component (a), 35 0 or 600 - 3,000 parts total component (b), 100 - 800 parts

component (c), 0 or 500 - 2,500 parts component (d), and 200 - 2,000 parts component (f) preferably by weight per million parts of polyolefin. Advantageously the component (d) consists of a mixture of a phosphite and a phosphonite details of the nature of which are 5 preferably as specified above with amounts in the stabilized polyolefin of 100 - 10,000 eg 300 - 1,500 ppm of the phosphite and 50 - 5,000 eg 200 - 1,000 ppm of the phosphonite, the total providing the 100 - 15,000 ppm of (d) quoted above. Very 10 advantageously the component (b) consists of the inorganic anion exchange compound, in amount of 10 - 10,000 eg 50 - 2,500 preferably 100 - 800 ppm of the polyolefin, or comprises such amounts with 0 - 10,000 eg 50 - 5,000 and especially 500 - 2,000 ppm of metal 15 carboxylate or metal oxide or hydroxide (as described above) to make the totals for (b) as described. Especially important are stabilizer compositions and stabilized compositions in which the 20 weight ratio of inorganic anion exchange compound (b) to deactivator (c) is 5:1 to 1:5 eg 3:1 to 1:4 preferably 2:3 to 1:3. The stabilizing effect of such mixtures of components (b) and (c) is synergistic, and at constant total weight is usually significant 25 better than the same weight of the component (b) or (c) alone, especially when there are 100 - 800 parts of each of the ion exchange compound (b) and deactivator (c), and in particular when these amounts are used to stabilize 1 million parts of polyolefin.

In another aspect therefore the present invention provides a 25 synergistic stabilizing mixture of an inorganic anion exchange compound (b) and a metal deactivator (c) (especially organic metal deactivator) in weight proportions of 5:1 to 1:5, and particular stabilized polyolefin compositions comprising polyolefin and 200 - 1,600 ppm of said mixture.

30 The stabilizer compositions of the invention may be made by blending the component in any order. The stabilized compositions may be made by blending the polyolefin with the stabilizer composition either premade and added as such or via one or more master batches, or preferably by blending the polyolefin with the 35 individual components of the composition added separately and melt

blended in a single or twin screw extruder, mixer or a batch mixer, preferably performed in a closed system with substantial exclusion of air.

5 The stabilizer and stabilized compositions of the invention may also contain conventional polyolefin additives such as for example processing aids, such as fluoropolymers, antistatic agents, antiblocking agents and anti slip agents, UV light absorbers, fibrous or non fibrous fillers dyestuffs and pigments.

10 Examples of fluoropolymer processing aids (component (f) above, are fluoro olefin homo or copolymer such as one based on a perfluoro ethylene or perfluoropropylene, such as tetrafluoro ethylene or hexa fluoropropylene, optionally with a fluoroolefin such as difluoro ethylene and/or a fluoro diene. The fluoropolymer is usually an elastomer and is often present in a fluoro composition in amount of 15 10 - 50% fluoropolymer, 0.1 - 10% of filler such as calcium carbonate and/or silica and/or barium sulphate and/or talc and 49.9 - 99.9% of liquid extender such as polyethylene glycol and/or solid extender such as a polyolefin. The presence of the fluoropolymer aids smooth passage through an extruder of the polyolefin to be 20 stabilized by the composition of the invention.

The stabilized composition may be moulded or extruded to form shaped articles such as fibres, pipes bottles and other containers, and films for use as such or in multicomponent laminates, or used for coating purposes.

25 The polyolefin composition of the invention may be extruded directly from a mixer/extruder or mixed first and formed into pellets, which may be subsequently remelted and extruded to form film. Examples of types of extruder are given above. The film may be obtained by extrusion through a slit die to form a flat film or 30 preferably through an annular die to form a molten tube and thence by blow moulding to form an expanded tube of film, which, if desired may be slit to form a flat film. The principles of production of film from slit or annular dies and by blow moulding are known methods (eg see Plastics Films by J H Riston, Publ Longman Group, 35 Harlow, Essex 1983 2nd Ed pp 67-73). But preferably the trapped

bubble technique is used in which the molten annular film leaving a die is expanded into a film tube of the desired diameter with gas entering through the die and maintained at the desired substantially constant pressure, the film tube being cooled, usually externally by blowing air against it. The cooled film tube is collected in guide rolls and thence at pinch rolls, to inhibit loss of internal gas pressure, and finally at wind up or haul off means. Films made from the polyolefin compositions of the invention comprising (a), (c) and (d) may have improved tear strength compared to those comprising components (a) and (d) and without the deactivator (c).

The invention is illustrated in the following Examples in which the following materials are used. The polyolefin was a linear low density polyethylene (LLDPE) of Spec. Gravity 0.922, Melt Index 0.9 g/10 mins measured according to ASTM D1238 Condition E), which was a copolymer of ethylene and butene; it contained about 20 ppm in total of titanium residues and about 100 ppm chloride ion. The hindered phenol (a) was pentaerythritol-tetra kis[3-(3,5-di tert.butyl-4-hydroxy phenyl) propionate] sold under the trademark IRGANOX 1010 by Ciba Geigy. The phosphite for (d) was tris(2,4-di-tert.butylphenyl) phosphite sold under the trademark IRGAFOS 168 by Ciba Geigy and the phosphonite was tetra kis-(2",4"-di-tert.butylphenyl)-4,4'-bisphenylene diphosphonite sold under the trademark IRGAFOS P-EPQ by Ciba Geigy. Anion exchange compound (b) was a dehydrotalcite (an Mg Al hydroxy carbonate) sold under the trademark DHT4A by Kyowa Chemical Industry Co Ltd (as described above) and neutralizer (b) was calcium stearate. Metal deactivator (c) was a phenolic oxamide (N,N<sup>1</sup>-bis[2-(3-[3,5 di tert.butyl-4-hydroxyphenyl] propionyloxy)ethyl] oxamide sold under the trademark NAUGARD XL-1 by Uniroyal. The fluoropolymer (f) was a fluorocopolymer from di-fluoroethylene and hexafluoropropylene monomers.

Ex 1-4

The ingredients were blended dry in the proportions quoted below and then mixed with molten polyolefin in a Haake RHEOCORD mixer with 46 g capacity mixing head, with 180 °C set head

temperature, rotor speed of 60 rpm and mixing time of 15 mins.

5 A nitrogen blanket over the top of the head and down the shafts of the rotors was used to prevent degradation of the polymer. All the additives were wrapped in an unstabilized polyethylene film envelope and then added with the LLDPE powder to the mixing chamber. Once blending was complete the material was removed from the mixer, quenched in water and dried in an oven. Small samples (6 mg) were cut from the blends and used to determine the melt stabilities as shown by the oxygen Induction Time (OIT) which is a 10 measure of the relative stability of a sample by indicating the time taken for a sample to oxidise at a particular temperature in this case 200 °C.

15 The test was performed by Differential Scanning Calorimetry in a duPont 1090 Thermal Analyzer, with measurement of the time taken between input of oxygen to the heated sample and the onset of the exothermic oxidation of the sample.

The results were as follows in which the amounts of additive are expressed as parts per million of the polyolefin.

Example 1 - 3

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Additive (Component)	Amount of Addition (ppm)				
	Comp. A	Comp. B	Ex 1.	Ex 2.	Ex 3.
25 Phenol (a)	300	300	300	300	300
Phosphite (d)	800	800	800	800	800
Phosphonite (d)	500	500	500	500	500
Ion Exchanger (b)	1000		500	250	500
Deactivator (c)		1000	500	500	250
30 OIT (Mins)	35	11	53	44	37

35 The results show the synergistic effect of the mixtures of ion exchanger (b) and deactivator (c) compared to the effect of an equal total weight of (b) or (c) alone.

Example 4

A modification of the composition of Ex 3. containing in addition 1000 ppm of neutralizer (b) calcium stearate and 700 ppm of fluoropolymer (f) was also made. The OIT value was 21 mins, while 5 without the deactivator the OIT value was only 9 mins.

Ex 5

The ingredients were blended dry in the proportions quoted below and then mixed with molten polyolefin in an extruder attached directly to a Betol film extrusion line. The extruder had 8 10 sections with an initial temperature profile of 180 °C and thereafter 190 °C, a screw diameter of 40 mm, and a rotor speed of either 150 or 300 rpm.

The molten polymer from the extruder passed at 10 kg/hr to a die and then into a Betol trapped bubble blow moulding film 15 production apparatus in which the polymer was extruded into a molten tube by an annular die, expanded into a film tube of 25 micrometres gauge by compressed air fed through the die centre, the film tube cooled externally to cause solidification with a frost line 60 mm above the air ring and the cooled tube guided by guide rolls, 20 collected by pinch rolls and wound up on a driven haul - up roller. The film was then tested for its Elmendorf tear strength by the technique of ASTM D1922.

The results were as follows with the amounts of additive expressed as parts per million of polyolefin and the Elmendorf Tear 25 Strength expressed in g/25 micrometres.

5	Additives ppm					Tear Strength on Film with Extruder Speed	
	Component	Phenol (a)	Phosphite (d)	Phosphonite (d)	Deactivator (c)	150 rpm	300 rpm
C	-	-	-	-	-	65.3	57.9
D	200	800	500	-	-	70.7	71.2
5	200	800	-	500	-	94.2	87.2

## Claims

1. A stabiliser composition which comprises (a) at least one phenolic or amine antioxidant and (c) a metal deactivator, and at least one of (b) a neutraliser and (d) an antioxidant which is a phosphorus containing compound or a thioether or sulphide.
- 5 2. A composition according to claim 1 wherein (c) is an organic compound with one pair of CONH or NHCO groups.
3. A composition according to claim 2 wherein (c) is an oxalamide or hydrazide.
- 10 4. A composition according to any one of the preceding claims wherein (b) if present is an inorganic anion exchanger in basic form.
5. A composition according to claim 4 wherein (b) if present is a magnesium aluminium talcite.
- 15 6. A composition according to any one of the preceding claims wherein the antioxidant (d) if present is a phosphonite or phosphite ester.
7. A composition according to any one of claims 1-3 and 6 which comprises (a) a phenolic antioxidant (c) an organic metal deactivator and (d) a phosphite or phosphonite ester or a mixture 20 thereof.
8. A composition according to claim 7 which comprises 50-5000 parts (a), 50-2500 parts of (c) and 200-7500 parts of (d).
9. A composition according to any one of claims 1-5 which comprises (a) a phenolic antioxidant (b) an inorganic neutraliser 25 and (c) an organic metal deactivator.

10. A composition according to claim 9 which comprises 50-5000 parts (a), 100-7500 parts (b) and 50-2500 parts of (c).
11. A composition according to claim 10 which also comprises 100-15000 parts of (d).
- 5 12. A stabilised polymer composition comprising a polyolefin and a stabiliser composition according to any one of the preceding claims.
13. A composition according to claim 12 wherein the polyolefin comprises at least one of transition metal and chlorine residues.
14. A film of a polymer composition according to claim 12 or 13.
- 10 15. A stabilising mixture of an inorganic anion exchange compound (b) and a metal deactivator (c) in weight proportions of 5:1 to 1:5.

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## Relevant Technical fields

(i) UK CI (Edition K ) C3K (KCZ, KCB, KCD, KCE, KCF, KCC, KCM, KCH, KCJ, KCL)  
 (ii) Int CL (Edition 5 ) C08K; C08L

## Search Examiner

B J BALDOCK

## Databases (see over)

(i) UK Patent Office  
 (ii) ONLINE DATABASE: WPI

Date of Search  
 15 APRIL 1992

## Documents considered relevant following a search in respect of claims

1 TO 14

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 1526466 (UBE) see Examples 1 to 11	1, 3, 12
X	GB 1490938 (CIBA-GEIGY) see page 4 line 9 to page 5 line 10	1, 3, 6, 7, 12
X	GB 1488076 (DART) see Claim 1	1, 3, 12
X	GB 1442266 (HERCULES) see whole specification	1, 3, 12
X, P	EP 0449685 A1 (SUMITOMO) (published 02.10.91) see Claim 1 and page 7 lines 25 - 27	1, 12
X	EP 0382559 A2 (TONEN) see Claims 1, 6-8, page 4 line 20 - page 5 line 20	at least 1, 12
X	EP 0276923 A2 (TONEN) see the whole specification	1, 4, 5, 6, 12
X	EP 0274200 A2 (UNIROYAL) see Examples 4, 6, 8, 10, 12 page 8 lines 6-32	1, 6, 12
X	EP 0184191 A2 (PHILLIPS)	1, 12
X	WO 82/02207 A1 (GEORG FISCHER) see whole specification	1, 3, 6, 7, 12

Category	Identity of document and relevant passages	Relevant to claim(s)

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(ii) Int CL (Edition) )

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## Documents considered relevant following a search in respect of claims

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	US 4829112 (SUMITOMO) see claims, column 3 lines 20-24	1, 6, 7, 12
X	US 4162247 (HOECHST) see Claim 3, column 4 lines 23-54	at least 1, 3, 12
X	US 4043976 (UBE) see Examples 1 to 4, 13 to 16, column 3 line 53 to column 4 line 57	at least 1, 3, 12
X	US 4012360 (CIBA-GEIGY) see Examples 11 to 24, Claims 6 to 9, column 3 line 33 to column 5 line 47	1, 3, 12
X	EP 0222566 A (SUMITOMO)	1, 3, 12
X	US 3894990 (CIBA-GEIGY) see whole specification	1, 3, 12
X	DD 000271337 A (VEB LEUNA-WERK)	1, 6, 7, 12
X	JP 082020354 B (ARGUS CHEM) see WPI Accession No:- 76-50434X/27	1, 3, 6, 7, 12

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## Relevant Technical fields

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## Databases (see over)

(i) UK Patent Office

(ii)

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## Documents considered relevant following a search in respect of claims

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	JP 081044918 B (ADEKA-ARGUS) see WPI Accession No: 75-853333W/52	1, 3, 6, 7, 12
X	US 3798286 (HERCULES) see Claims 1 to 4 and Example	1, 3, 12
X	US 0914009 T (BROWN W FARBER)	1, 3, 12

Category	Identity of document and relevant passages	Relevant to claim(s)

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